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SYNTHESIS GAS UTILIZATION AND PRODUCTION IN A BIOMASS LIQUEFACTION FACILITY

C. Figueroa and S. Ergun

November 1979

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SYNTHESIS GAS UTILIZATION AND PRODUCTION IN A BIOMASS LIQUEFACTION FACILITY

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November 1979

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ABSTRACT

A novel approach towards a combination biomass liquefaction and gasification process scheme is examined. The reactor arrangement is basically a liquefaction tubular coil reactor internally installed into a pressurized oxygen-blown Lurgi type gasifier. The potential for a dual purpose reactor is excellent due to lower capital costs.

Advantages include: high radiant heat transfer, small reactor size, smaller compressor size, and a self-contained heating system for liquefaction. Disadvantages include: added capital costs for carbon dioxide removal and gas scrubbing. Without any energy recovery or mass recycle (CO_2) the thermal efficiency would be poor, perhaps as low as 51%.

SYNTHESIS GAS UTILIZATION AND PRODUCTION IN A BIOMASS LIQUEFACTION FACILITY

I. INTRODUCTION

The requirement for reducing gases, mixtures of carbon monoxide and hydrogen, for biomass liquefaction processes has been demonstrated by PETC, PNL and LBL researchers. Quantities of the reducing or synthesis gas must be supplied on an as needed basis, therefore the need for a continuous biomass gasification unit.

The selection basis for a particular gasifier can be determined by the following:

- CO/H_2 ratio and production requirements
- Biomass feed physical and chemical characteristics
- Non-gasification uses:
  - (1) for internal heat recovery, such as the insertion of the primary liquefaction reactor coil into the gasifier
  - (2) for catalyst (slag) recovery and recycle
- Capital and operating costs

Careful examination of these factors can lead to the most promising process configuration for biomass liquefaction.

II. DISCUSSION

2.0 Gasifier Selection

The selection process for a particular gasification unit begins with the synthesis gas requirements. For a sodium carbonate catalyzed biomass liquefaction system, carbon monoxide has been determined to be the principal gas reactant through unpublished results by Guy,(1) Seth, and Ergun.(2) This primary requirement obviously leads to high temperature gasification operation for which carbon monoxide formation is favored through the water-gas shift reaction. However, at the present time it does not appear that the optimum ratio of hydrogen to carbon monoxide needed in biomass liquefaction has not been established.

2.1 Fluidized and Fixed Bed Gasifiers

The advantages and disadvantages of fluidized-bed and fixed-bed gasifiers must be examined for high temperature operation. To begin with, fluidized-bed gasifiers do have an advantage in that near water-gas shift equilibrium can be obtained. However, there are added process costs associated with high temperature fluidized-bed entrainment such as the recycling of solids carryover and water treatment due to water scrubbing of high boiling point oils and tars from the product gas stream.

2.2 Gasifier Feedstock

Entrainment is a function of the biomass feedstock physical and chemical characteristics. Under fluidization conditions one would expect considerable carryover of low density material such as crop residues, wood by-products, municipal refuse, etc. It is possible, however, to circumvent the low density feed problem through densification of the feed which requires partial drying. After an initial drying process step, densification would include pelletizing, cubing, briquetting, extrusion, and rolling and compressing. The obvious disadvantage of densification is the added feed processing costs. Weighing the above mentioned factors against a simple low-entrainment fixed-bed unit, the fixed-bed gasifier appears to be more cost effective.

2.3 Co-Current/Counter-Current Gasifiers

Co-current fixed-bed gasifiers can be ruled out for the simple fact that elevated temperatures cannot be achieved for practical CO production if high CO/H_2 ratio is needed. A counter-current gasifier appears to be the best choice. In addition, a low product gas outlet temperature is desireable for the purpose of minimizing the carryover of tars and oils. This would result in reduced gas scrubbing processing costs as well as associated water treatment costs.

2.4 Air and Oxygen Blown Gasifiers

Air and oxygen blown gasifiers are compared as they affect the liquefaction process step. An air-blown gasifier would certainly be less expensive to operate over an oxygen blown system, but the drawbacks of introducing a nitrogen-rich synthesis gas stream into the liquefaction stem can be summarized as follows:

(1) Nitrogen can act as a diluent, thus reducing reaction rates. The presence of nitrogen decreases the biomass throughput rate.

(2) The effective heat transfer can be low in a liquefaction tubular reactor due to a high gas-to-liquid ration.

Compared to pure oxygen usage, air will result in a five-fold increase in the superficial gas velocity which could present problems such as bed slugging, Channelling, and entrainment. Therefore, it is concluded that an oxygen-blown fixed-bed gasifier is best.

From the view point of an integrated liquefaction and gasification system, the emphasis must be placed on process configuration and, in particular, to the design of respective reactors.

2.5 Gasifier/Liquefaction Process Configuration

The elevated temperatures produced within the gasifier certainly might provide the energy requirements for the liquefaction tubular reactor. Conceptually, improper heat removal from the gasifier could prove to be a problem such as quenching desireable gasification and pyrolysis reactions. By the same token, heat removal might be beneficial by quenching gases after the gasification zone in the bed, thereby effectively freezing the water-gas shift equilibrium produced in the gasification zone. Since CO formation is favored at elevated temperature, this process configuration will serve to maximize CO production for a fixed bed gasifier.

Internal heat transfer in the gasifier can be greatly enhanced if it is operated at elevated pressures. In other words, the resulting increase in gas density improves the transference of energy from the gas phase to the internal liquefaction coils. Such an arrangement is shown for a Lurgi-type gasifier in Figure 1.

Other advantages of pressurized gasifier operation include:

(1) Reduced oxygen consumption due to enhanced mass transfer by increased oxygen concentrations.

(2) Lower superficial gas velocity resulting in a smaller stable bed depending upon the pressure chosen.

(3) Lower capital costs due to a smaller vessel requirement.

(4) Reduced compressor costs for pressurized CO_2 removal systems such as the hot potassium carbonate/formate method or for direct injection of synthesis gas into the liquefaction reactor.

One disadvantage is that the downstream gas scrubbing vessels must be pressure vessels which results in an incremental capital cost increase for those particular vessels.

The gasifier shown in Figure 1 is integrated into a liquefaction plant flow scheme shown in Figure 2. Biomass or logged wood chip, in this case, is charged to the gasifier through a feed hopper. The resulting synthesis gas is water quenched for cooling and removal of any oils and tars. If necessary, CO_2 is removed from the synthesis gas stream as previously discussed, the resulting CO/H_2 mixture is compressed and injected into the liquefaction reactor. The removed CO_2 can be either recycled back to the gasifier or vented. Recycling CO_2 will maximize CO production.

A pressurized slurry of pretreated hydrolyzed biomass, water, and sodium carbonate is combined with the CO/H_2 gas mixture and sent to the liquefaction reactor coil which is located in the pyrolysis zone of the gasifier. The resulting oil/water/gas product is reduced in pressure through a two-stage flash tank arrangement as shown in Figure 2. Steam from these two flash tanks can be utilized for process heating requirements. Water is separated from the product oil through a standard decanting oil/water separator. The catalтst bearing oil stream is indirectly heated and sent to a vacuum flash distillation column where the distillable oil is condensed, collected, and transported for use.

FIGURE 1

Modified Lurgi Gasifier with Liquefaction Reactor

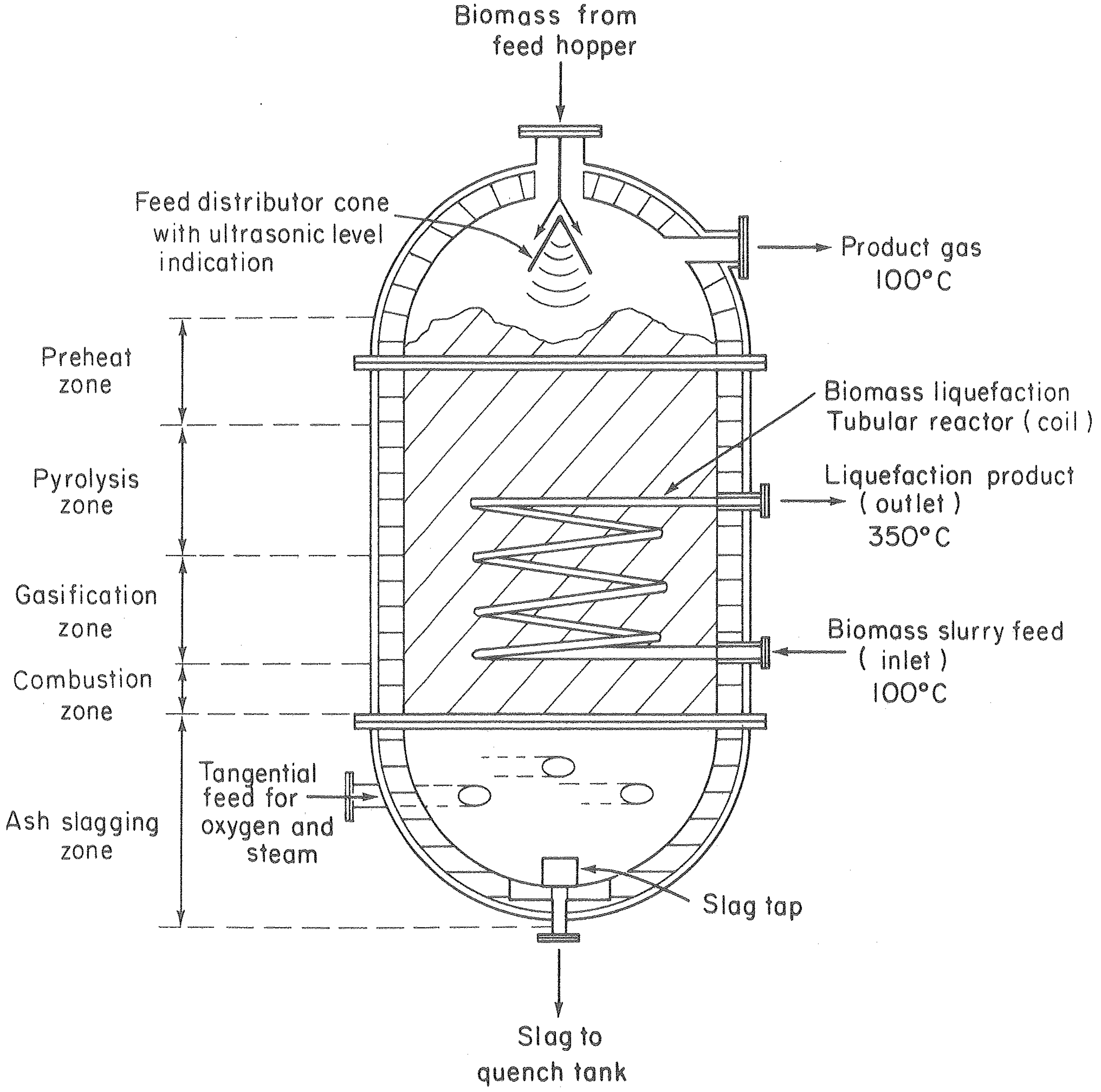
Biomass from feed hopper
Feed distributor cone with ultrasonic level indication
Product gas 100°C
Preheat zone
Pyrolysis zone
Gasification zone
Combustion zone
Ash slagging zone
Biomass liquefaction Tubular reactor (coil)
Liquefaction product (outlet) 350°C
Biomass slurry feed (inlet) 100°C
Tangential feed for oxygen and steam
Slag tap
Slag to quench tank

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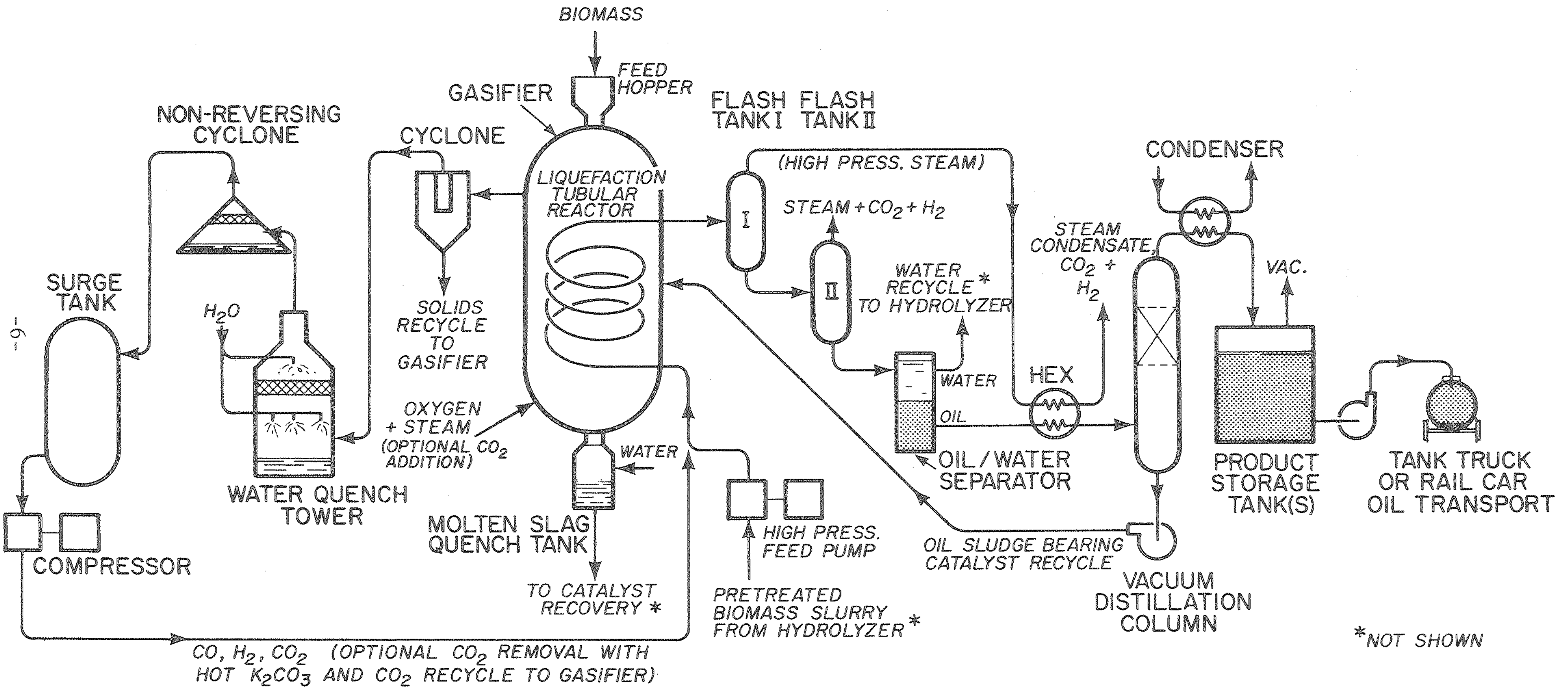
FIGURE 2

Conceptual Commercial Biomass Liquefaction Flow Schematic
LBL Process


BIOMASS
FEED HOPPER
GASIFIER
NON-REVERSING CYCLONE
CYCLONE
LIQUEFACTION TUBULAR REACTOR
FLASH TANK I
FLASH TANK II
(HIGH PRESS. STEAM)
I
II
STEAM + CO_2 + H_2
CONDENSER
STEAM CONDENSATE, CO_2 + H_2
WATER RECYCLE TO HYDROLYZER *
VAC.
SURGE TANK
H_2O
SOLIDS RECYCLE TO GASIFIER
WATER
HEX
OIL
OXYGEN + STEAM (OPTIONAL CO_2 ADDITION)
WATER
OIL/WATER SEPARATOR
PRODUCT STORAGE TANK(S)
TANK TRUCK OR RAIL CAR OIL TRANSPORT
WATER QUENCH TOWER
MOLTEN SLAG QUENCH TANK
HIGH PRESS. FEED PUMP
OIL SLUDGE BEARING CATALYST RECYCLE
VACUUM DISTILLATION COLUMN
COMPRESSOR
TO CATALYST RECOVERY *
PRETREATED BIOMASS SLURRY FROM HYDROLYZER *
*NOT SHOWN
CO, H_2, CO_2 (OPTIONAL CO_2 REMOVAL WITH HOT K_2CO_3 AND CO_2 RECYCLE TO GASIFIER)

XBL 7910-4542

The column bottom stream contains catalyst and oil residue which is recylced back to the gasifier for residue combustion and catalyst recovery. Under gasifier reducing conditions the sodium salts are regenerated back to sodium carbonate and tapped as a molten slag where it is water quenched and recycled as a 20% catalyst solution.

3.2 Liquefaction Reactor Design Basis

Heating a liquefaction coil inside a gasifier is not an entirely new idea. Considerable work has been performed on heat transfer in fixed bed system. (3) The most interesting item to come out of this work is the fact that radial heat transfer can be promoted in a gas-solid system. Aside from solid-to-solid radiant heat transfer, radial heat transfer is excellent due to the disruption of the laminar sub-boundary layer by the presence of solids against the primary heat transfer surface. A relationship developed by Smith, J.M. (3) related the heat transfer coefficient to the bed characteristics:

$$h = \frac{3.5\ ke}{D_t}^{-4.6\ D_p/D_t} \left(\frac{D_p S \bar{u}_s}{\mu} \right)^{0.7} \quad (=)\ \text{Btu/H}^2\ \text{hr}\ {}^{\circ}\text{F}$$

where,

k = gas thermal conductivity (=) Btu-ft/$_{\text{ft}^2}$ hr$^{\circ}$F

D_p = particle diameter (=) ft

D_t = vessel diameter (=) ft

$\bar{u}_s$ = superficial velocity (=) ft/sec

Other reactor design parameters include the following:

(1) The internal wall temperature must not exceed 850°F in order to avoid coking.

(2) The Reynolds number must be well above 2000.

(3) An acceptable heat flux is 9000 Btu/ft^2 hr$^{\circ}$.

(4) Steam generation must be taken into consideration as it will be a function of the overall pressure temperature and synthesis gas flow input.

(5) A minimum of 20 minute residence for the reaction mixture is recommended.

Given the above design parameters, the coil sizing is relatively straightforward.

III. GASIFICATION/LIQUEFACTION DESIGN BASIS

3.0 Biomass Feedstock

As harvested, green biomass typically contains an average of 50% moisture, Douglas fir in this case. The moisture content can be reduced to 23% by providing a 30-day stock piling of the green biomass as the pile will undergo spontaneous internal heating caused by respiration and other reactions.(4) By minimizing the moisture content, less oxygen is required to maintain proper gasification temperatures. Desrosiers (5) has examined this approach and outlined 'front-end handling' system for a gasification facility. His recommendations include further research for the optimization of biomass pile height, residence time, and final moisture content. When such a study is performed, other factors must be taken into account such as biomass seasonal availability, inventory penalties, or general economic considerations. A reasonable size for a liquefaction plant is taken at 6680 TPD dry biomass. 90 days of inventory is assumed for regions with extended winter seasons. Of the total biomass feed, 75% is sent to the liquefaction section, 14% is gasified to CO H_2 and the remaining 11% is combusted in the gasifier to supply process heat to the liquefaction coil. These calculations are outlined in Appendix A. This is a worst case calculation where no mass or energy recycles are taken into consideration. The minimum plant energy efficiency is calculated at 51%.

3.1 Gasification Reaction Basis

A simple approach to the gasification system is outlined. As previously discussed, a liquefaction coil is inserted into a Lurgi-type fixed-bed, oxygen-blown, pressurized gasifier. The major assumption made is that the coil will freeze the water-gas shift equilibrium from the gasification zone. Therefore, the gasifier stiochiometry can be broken into two parts:

(1) The gasification reaction necessary to supply a specified quantity of carbon monoxide to the liquefaction ractor.

(2) The combustion reaction necessary to supply the process heat to the liquefaction reactor.

The overall reaction, as determined from Appendix A, follows:

$$CH_{1.4}O_{0.59} + 0.64O_2 + 0.38\ H_2O =$$

$$0.32\ H_2 + 0.76\ H_2O + 0.51\ CO + 0.49\ CO_2.$$

The quantities of CO_2 generated from this reaction scheme necessitates the need for CO_2 removal so as to avoid dilution of the synthesis gas.

IV. SUMMARY

To date, an optimal process scheme for general biomass liquefaction has not been decided upon as there are numerous biomass feedstocks to explore. Different feedstock will perhaps require varying front-end handling techniques, gasification conditions, and even different liquefaction conditions.

For the case considered in this report, Douglas fir wood, our best conceptual process scheme is a combined liquefaction/gasifier arrangement. Advantages for this particular scheme are as follows:

- high radial heat transfer
- small reactor size
- reduced compressor costs
- reduced water treatment costs

Disadvantages include increased capital costs for CO_2 removal and gas scrubbing equipment.

A worst case calculation for plant efficiency was made with no mass or energy recycles thus giving a minimum plant efficiency of 51%.

APPENDIX

GASIFIER/LIQUEFACTION DESIGN CALCULATION

Design Basics

- o Reaction Stiochiometry:

(1) Gasification @ 1500°K + 300 psig (Ref. 5)

$CH_{1.4}O_{0.50} + 0.29\ O_2 = 0.6\ H_2 + 0.1\ H_2O + 0.94\ CO + 0.06\ CO_2$

(Wood) (Ref. 3)

(2) Liquefaction @ 620°K + 3000 psig

$CH_{1.4}O_{0.59} + 0.17\ CO \overset{(Na_2CO_2)}{=} \text{Wood oil} + CO_2$

- o Feedstock conditions:

(1) Green wood chips contain 50% moisture

(2) Piles of green biomass can reach a equilibrium moisture content of 23% after one month. (Ref. 5)

- o Liquefaction Reactor Biomass Feed

(1) 5000 TPD (dry biomass)

Gasifier Wood Feed for CO Production

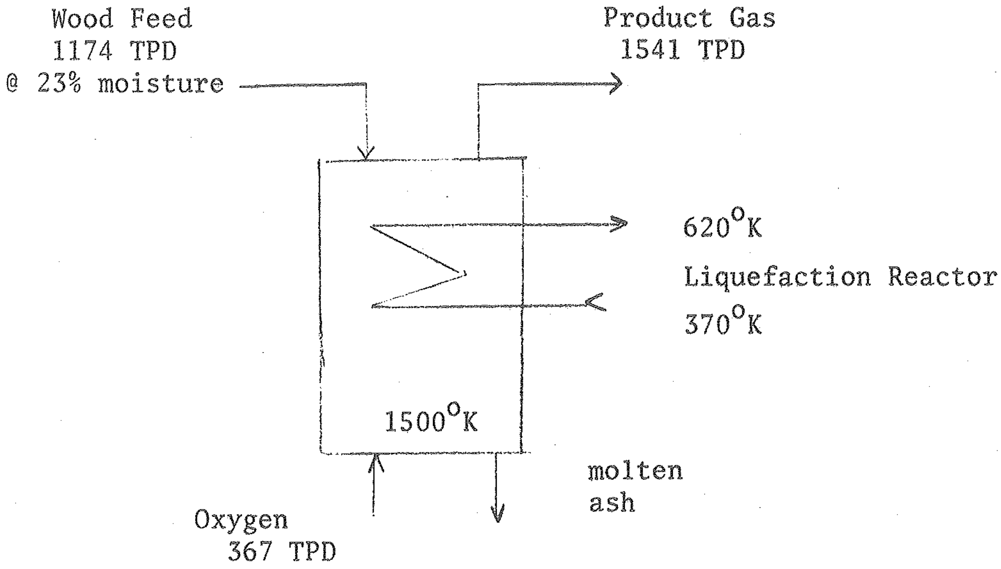
- o Wood Feed = $(5000\ \text{TPD}) \dfrac{0.17\ \text{mole CO}}{1\ \text{mole wood}} \dfrac{1\ \text{mole wood}}{0.94\ \text{CO}}$

(GAS) (LIQ)

= 904 TPD Dry Biomass

or = 1174 TPD @ 23% moisture

o Mass Balance (Preliminary)


Wood Feed
1174 TPD
@ 23% moisture
Product Gas
1541 TPD
620°K
Liquefaction Reactor
370°K
1500°K
molten
ash
Oxygen
367 TPD

o Product Gas Composition (Basis: 1 mole wood)

	moles	mole %	wt %
H_2	0.6	29%	3.1%
H_2O	0.1	23%	22.3%
H_2O	0.38 (moisture)	-	-
CO	0.94	55%	67.8%
CO_2	0.06	3%	6.8%
	2.08	100%	100

o Energy Balance (Preliminary)

(1) Heating Value of wood @ 9000 Btu/lb

$$H_V = (9000 \text{ Btu/lb})\ (904 \text{ TPD}) \left(2000 \text{ lb}/_{T}\right)$$

$$= 1.63 \times 10^{10} \text{ Btu/Day}$$

(2) Heating value of $CO + H_2$

$$CO: \quad (4{,}347)\ \text{Btu/lb})\ (1541\ \text{TPD})\ (0.678)\ \ 2000\ \text{lb}/_{T}$$

$$H_2: \quad (61{,}100\ \text{Btu/lb})\ (1541\ \text{TPD})\ (0.031)\ \ 2000\ \text{lb}/_{T}$$

$$= \underline{5.84 \times 10^{9}\ \text{Btu}/_{\text{Day}}}$$

$$\text{Total Energy Value} \quad = 1.49 \times 10^{10}\ \text{Btu}/_{\text{Day}}$$

(3) Gasifier Energy Efficiency

$$G_E = \frac{1.49 \times 10^{10}\ \text{Btu}/_{\text{Day}}}{1.63 \times 10^{10}\ \text{Btu}/_{\text{Day}}} = 100$$

$$= 91.4\%$$

o Liquefaction Energy Requirements

Feed Composition:		wt %
Biomass	5000 TPD	37%
H_2O	7500 TPD	55%
$CO/_{H_2}$	1092 TPD	8%
	13,592 TPD	

(1) Energy required to raise feed temperature

from 100°C to 350°C or $\Delta T = 250^{\circ}C$

$$E_R = (12{,}500\ \text{TPD})\ (250^{\circ}C)\ (^{2000}\ \text{Btu}/_{T}\ {}^{\circ}F)\,(^{1.8}\,{}^{\circ}F/_{{}^{o}C})$$

$$+ (1092\ \text{TPD})\ (250^{\circ}C)\,(^{500}\ \text{Btu}/_{T}{}^{\circ}F)\,(1.8\ {}^{\circ}F/_{{}^{o}C})$$

$$= (1.125 \times 10^{10}\ \text{Btu}/\text{Day} + 2.457 \times 10^{8}\ \text{Btu}/\text{Day}$$

$$= \underline{1.15 \times 10^{10}\ \text{Btu}/\text{Day}}$$

(2) Additional Wood Feed Required to Gasifier

$$W_f = \frac{1.15 \times 10^{10}\ \text{Btu}/\text{Day}}{(9000\ \text{Btu}/_{\text{lb}})\ (2000\ \text{lb}/_{t})}$$

$$= 639\ \text{TPD}$$

o Water vaporized during liquefaction

P_{H_2O} @ 620°k = 2200 psig

Partial pressure of CO/H_2 = 800 psig

(by difference)

Therefore, water vaporized = W_v

$W_v = (\frac{2200}{800})$ 84 lb-moles/min = 231 lb-moles

or = 2721 TPD wafer vaporized

@ 450 Ctu/lb heat of vaporization

$H_v = 2.45 \times 10^9$ Btu/Day

Additional wood to gasifier required

$$W_g = \frac{2.45 \times 10^9 \ Btu/day}{(9000\ Btu/lb)(2000\ \frac{lb}{t})}$$

= 136 TPD

o Total Additional Wood = 136 + 639 = 775 TPD

o Mass Balance (Final)

$CH_{1.4}\ O_{o.59} = 1.055\ O_2 = CO_2 = 0.7\ H_2O$

1) Additional O_2 required = $(CO_2 = H_2)$ produced

O_2 : 1146 TPD

CO_2 : 1493 TPD

H_2O : 428 TPD (1) By Reaction

H_2O : 231 TPD (2) By moisture content

Additional Product Gas Moss = 2152 TPD

Overall Reaction : (Ton mole/Day Basis)

1) Gasification

$$39.58\ CH_{1.4}\ O_{0.59} = 11.48\ O_2 + 15\ H_2O = 23.75\ H_2 + 18.96\ H_2O + 37.21\ CO + 2.37\ CO_2$$

2) Combustion

$$33.93\ CH_{1.4}\ O_{0.59} \overset{+12.83\ H_2O}{+ 35.80\ O_2{}^{v}} = 33.93\ CO_2 + 36.61\ H_2O$$

Combine 1) and 2) ;

47.28

3) $73.51\ CH_{1.4}O_{0.59} + v\ O_2 + 27.83\ H_2O =$

$23.75\ H_2 + 55.57\ H_2O + 37.21\ CO + 36.30\ CO_2$

Simplify to a unit carbon basis;

4) $CH_{1.4}O_{0.59} + 0.64\ O_2 + 0.38\ H_2O =$

$0.32\ H_2 + 0.76\ H_2O + 0.51\ CO + 0.49\ CO_2$

o Product Gas Composition: (mole %)

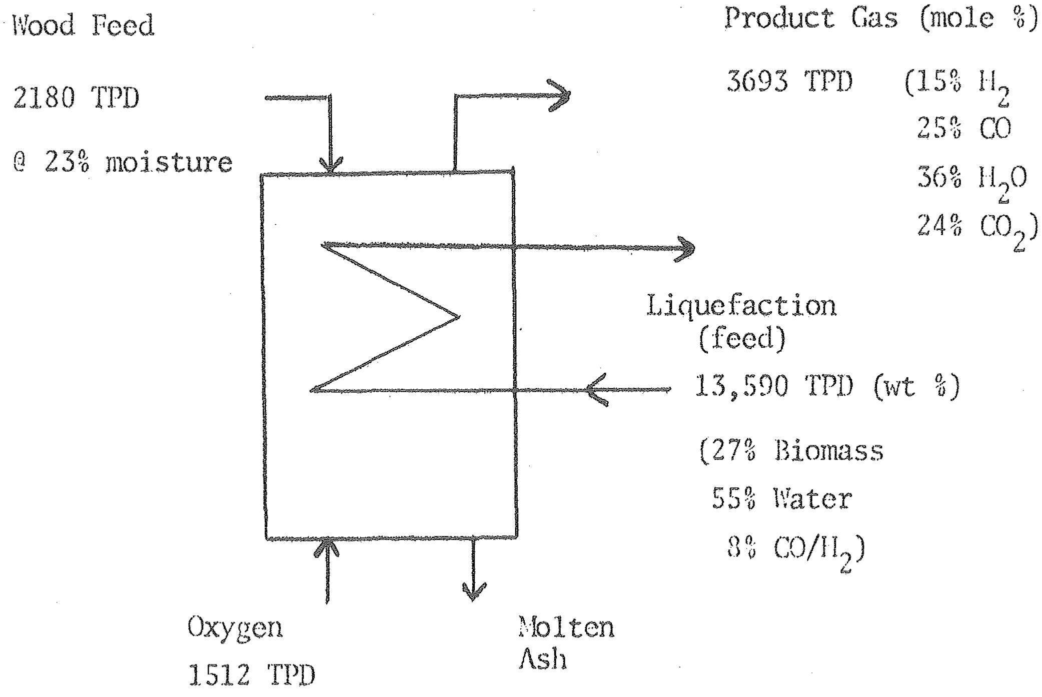
H_2 : 0.32 = 15%

H_2O : 0.76 = 36%

CO : 0.51 = 25%

CO_2 : $\underline{0.49}$ = 24%

2.08


Wood Feed
2180 TPD
@ 23% moisture
Product Gas (mole %)
3693 TPD (15% H_2
25% CO
36% H_2O
24% CO_2)
Liquefaction
(feed)
13,590 TPD (wt %)
(27% Biomass
55% Water
8% CO/H_2)
Oxygen
1512 TPD
Molten
Ash

REFERENCES

1. Donaruma, L.G., "Conversion of Organic Wastes to Oil by Reductive Formylation," Presented at the Engineering Foundation Conference on Resource Recovery, New England College, Henniker, New Hampshire, July 1979.

2. Seth, M., Unpublished data, Lawrence Berkeley Laboratory, University of California, 1979.

3. Lowry, H.H., "Chemistry of Coal Utilization," Chapter 20, Coal Gasification, Von Fredersdorff, C.G. (IGT) p. 892, John Wiley and Sons, Inc., New York 1963.

4. SERI Report "A survey of Biomass Gasification," Department of Energy Contract No. EG-77-C-01-4042, July 1979.

5. Desrosiers, R.E., "Process Designs and Cost Estimates for a Medium BTU Gasification Plant Using A Wood Feedstock," SERI Report to the Department of Energy under Contract No. EG-77-C-01-4042, February 1979.

BIBLIOGRAPHY

1. Wan, E.I., "Comparison of Thermochemical Gasification Technologies for Biomass," Presented at the Symposium on Energy from Biomass and Wastes, August 14, 1978, Washington, D.C.

2. Antal, M.J., Jr., "Effects of Residence Time, Temperature and Pressure on the Steam Gasification of Biomass," Department of Energy Contract No. ET-78-F-02-5058, Presented at ACS National Meeting, Honolulu, Hawaii, April 1, 1979.

3. Atomics International (Rockwell) Proposal to Department of Energy, "Catalytic Steam Gasification of Biomass," April 28, 1978.

4. Liu, M.S., "Fluidized Bed Solids Waste Gasifier," Forest Products Journal, Vol. 26, No. 9, p. 56, 1976.